Sodium Ion Binding to Cationic Surfactants in Micellar Systems – a ^{23}Na NMR Study

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^{23}Na NMR spectroscopy

I = 3/2, 100% abundant, Larmor Frequency = 79.4MHz at 7.0T.

For $Na^+_{(aq)}$, quadrupole relaxation dominates the spin lattice relaxation.

In the extreme narrowing limit :

$$\frac{1}{T_1} = R_1 = \frac{2\pi^2}{5}\left(\frac{e^2qQ}{h}\right)^2\tau_c$$

T_1: spin-lattice relaxation time (s)
R_1: spin-lattice relaxation rate (s^{-1})
eq: eletric field gradient (V m^{-2})
eQ: nuclear quadrupole moment (C m^2)
τ_c: correlation time (s)

Binding model:

$$[Na^+] + [L^-] \rightleftharpoons [NaL]$$

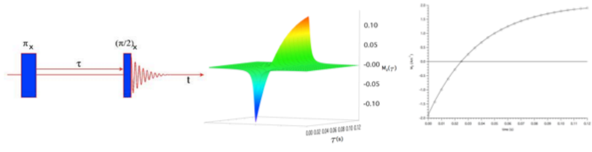
$$K_{formation} = \frac{[NaL]}{[Na^+][L^-]} \qquad [Na^+] + [NaL] = [Na^+]_{total}$$

$$X_{free} = \frac{[Na^+]}{[Na^+]_{total}} \qquad X_{bound} = \frac{[NaL]}{[Na^+]_{total}} \qquad X_{free} + X_{bound} = 1$$

In the fast chemical exchange limit, the observed relaxation rate is given by weighted average:

$$R_{1,observe} = R_{1,free}X_{free} + R_{1,bound}X_{bound}$$

T_1 measurement by inversion recovery:

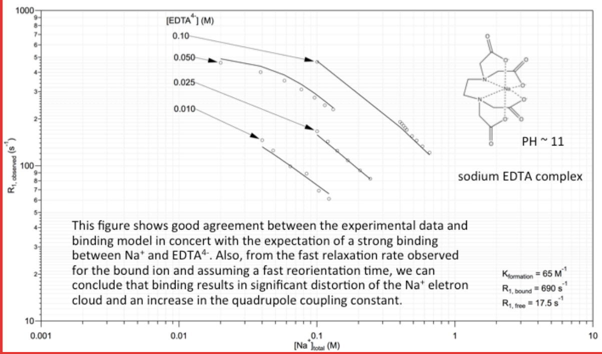


Analysis of the observed signal amplitude as a function of inversion recovery time (τ) yields the relaxation time:

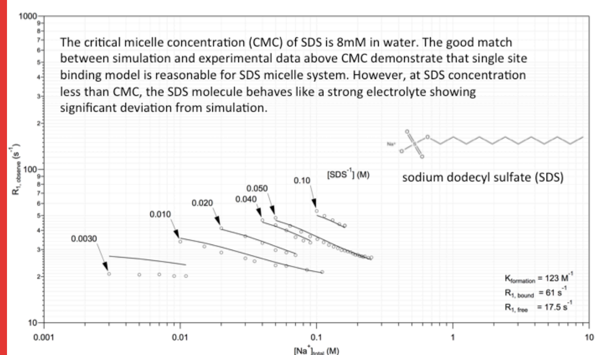
$$M_Z(\tau) = M_Z(\infty)\left(1 - (1+\alpha)e^{\frac{-\tau}{T_1}}\right)$$

α: inversion efficiency (≤ 1)

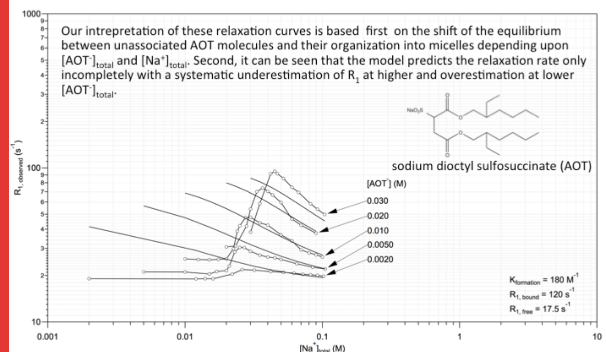
M_z: magnetization along z-axis



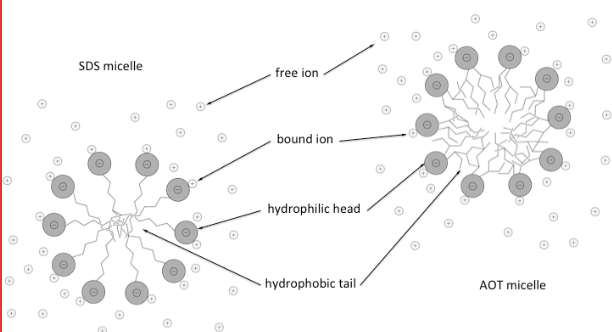
This figure shows good agreement between the experimental data and binding model in concert with the expectation of a strong binding between Na^+ and $EDTA^{4-}$. Also, from the fast relaxation rate observed for the bound ion and assuming a fast reorientation time, we can conclude that binding results in significant distortion of the Na^+ eletron cloud and an increase in the quadrupole coupling constant.



The critical micelle concentration (CMC) of SDS is 8mM in water. The good match between simulation and experimental data above CMC demonstrate that single site binding model is reasonable for SDS micelle system. However, at SDS concentration less than CMC, the SDS molecule behaves like a strong electrolyte showing significant deviation from simulation.



Our intrepretation of these relaxation curves is based first on the shift of the equilibrium between unassociated AOT molecules and their organization into micelles depending upon $[AOT^-]_{total}$ and $[Na^+]_{total}$. Second, it can be seen that the model predicts the relaxation rate only incompletely with a systematic underestimation of R_1 at higher and overestimation at lower $[AOT^-]_{total}$.



Measuring micellar rotational correlation time by ^{2}H NMR:

As R_1 depends on both the effective quadrupolar coupling constant (e^2qQ) and molecular reorientation time (τ_c), an independent measurement of one of these parameters is required. We shall use specifically labeled AOT and ^{2}H quadrupolar NMR spectroscopy to independently measure τ_c. The quadrupole relaxation mechanism dominates ^{2}H spectroscopy. When the ^{2}H atom is attached to a carbon atom close to the head group, its motion is expected to be representative of the overall motion of entire micelle.

Labeled AOT molecule: